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# CHEMICAL AMPLIFICATION TYPE POSITIVE RESIST COMPOSITION

The present invention relates to a chemical amplification type positive resist composition used for a fine processing in a production of semiconductors.

A lithography process using a resist composition is normally employed for a fine processing in a production of semiconductors. In lithography process, as shown by the Rayleigh's formula of diffraction limit, the shorter the exposure wavelength, the more the resolution can be increased in principle. Regarding an exposure light source for lithography used for producing semiconductors, its wavelength is decreasing every year. That is, before g-ray with a wavelength of 436 nm, which had been widely used, was replaced by i-ray with a wavelength of 365 nm and then, i-ray is being replaced by KrF excimer laser with a wavelength of 248 nm. As the exposure light source for next generation, ArF excimer laser with a wavelength of 193 nm is being hopefully considered.

Since lens used in an ArF excimer laser aligner has a life time shorter than that of an aligner using conventional exposure light source, shorter time for exposure of ArF excimer laser is desired. It is necessary to enhance the sensitivity of a resist to decrease the exposure time. Therefore, a so-called chemical amplification type resist, which utilizes a catalytic action of the acid generated by the exposure and contains a resin having a group cleavable by an action of the acid, is preferably used.

It is known that a resin having no aromatic ring but having

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an alicyclic ring in place of the aromatic ring is preferred for using in the resist for ArF excimer laser exposure in order to secure light transmission of the resist and to impart the dry etching resistance. As such a resin, various resins, such as those described in D.C. Hofer, Journal of Photopolymer Science and Technology, Vol. 9, No. 3 (1996) 387-398, have hitherto been known. However, a conventional known resin has a problem that peeling at the time of developing is liable to be caused due to lack of the adhesion at developing, particularly when the resin lacks the polarity.

An object of the present invention is to provide a chemical amplification type positive resist composition comprising a resin component and an acid generator, which is suitable for excimer laser (e.g. ArF laser, KrF laser, etc.) lithography, and which is good in various resist performances such as sensitivity and resolution and is particularly good in adhesion to a substrate.

The present inventors have found that the adhesion of a chemical amplification type positive resist composition to a substrate is improved by introducing a certain group into a resin comprised in the resist composition. Thus, the present invention has been accomplished.

The present invention provides a chemical amplification type positive resist composition comprising a resin having a butyrolactone residue which may be optionally substituted with an alkyl as well as a group capable of cleaving by an action of an acid, and an acid generator.

The resin comprised in the resist composition of the present invention is normally produced by polymerizing or copolymerizing a compound having an ethylenically unsaturated bond. It is preferred that the resin has no aromatic ring but has an alicyclic ring. The alicyclic ring is preferably an alicyclic hydrocarbon residue, particularly the alicyclic hydrocarbon residue having a crosslinked hydrocarbon ring. Examples of the alicyclic ring include bornane ring, norbornane ring, tricyclodecane ring, tetracyclododecane ring and adamantane ring. Examples of the compound having an ethylenically unsaturated bond, i.e. the monomer unit from which the resin is produced, include a compound derived from an alicyclic ester of (meth)acrylic acid and a compound derived from a vinyl or isopropenyl ester of an alicyclic carboxylic acid.

The resin comprised in the resist composition of the present invention has a butyrolactone residue in it. The butyrolactone residue includes not only an unsubstituted butyrolactone residue but also a butyrolactone residue substituted with an alkyl. Example of the alkyl include those having about 1 to 4 carbon atoms, i.e. methyl, ethyl, propyl, butyl and the like. The butyrolactone residue may be linked to the resin base via an ester or ether linkage. The position in the butyrolactone residue which links to the resin base is not specifically limited. For example, it may be the  $\alpha$ -position (i.e. 2-position) of butyrolactone.

The resin comprised in the resist composition of the present invention may comprise both a polymerization unit which

has an alicyclic ring and a polymerization unit which has a butyrolactone residue. The resin may also comprise a polymerization unit which has both an alicyclic ring and a butyrolactone residue. For example, the polymerization unit  
5 may be derived from the alicyclic ester of (meth)acrylic acid, wherein the butyrolactone residue is linked to the alicyclic ring via an ester or ether linkage.

The butyrolactone residue may be introduced into the resin base after the resin base was produced, or may be introduced into  
10 the monomer unit which is, then, polymerized to produce the resin.

The butyrolactone residue may be introduced into the resin or the monomer unit, for example, by converting a carboxylic group present in the resin into a butyrolactone ester or converting an alcoholic hydroxyl group present in the resin into a  
15 butyrolactone ether. In the esterification or etherification, for example, there can be used a halogen-substituted substance of butyrolactone which may be optionally substituted with an alkyl. Examples of the monomer unit into which a butyrolactone residue is introduced include  $\alpha$ -acryloyloxy- $\gamma$ -butyrolactone,  
20  $\alpha$ -methacryloyloxy- $\gamma$ -butyrolactone,  $\alpha$ -acryloyloxy- $\beta$  and  $\beta$ -dimethyl- $\gamma$ -butyrolactone.

The resin for chemical amplification type resist is insoluble or slight-soluble in an alkaline as it is, but a part of groups is cleaved by an action of an acid and the resin becomes  
25 alkaline-soluble after cleaving. Therefore, the resin used in the present invention has a group capable of cleaving by an action of the acid, in addition to the butyrolactone residue. The group capable of cleaving by an action of the acid may contain an

alicyclic ring mentioned above.

The group capable of cleaving by an action of the acid is known in the field of the resist. Examples thereof include alkyl group branched at the 1-position, such as tert-butyl; 5 optionally substituted 1-alkoxyalkyl group such as 1-ethoxyethyl, 1-(2-methoxyethoxy)ethyl, 1-(2-acetoxyethoxy)ethyl, 1-[2-(1-adamantyloxy)ethoxy]ethyl and 1-[2-(1-adamantanecarbonyloxy)ethoxy]ethyl; and residue of a non-aromatic cyclic compound, such as tetrahydro-2-furanyl, 10 tetrahydro-2-pyranyl, 3-oxocyclohexyl, 4-methyltetrahydro-2-pyrone-4-yl (derived from mevalonic lactone) and 2-methyl-2-adamantyl.

The group capable of cleaving by an action of the acid, such as those mentioned above, are introduced into the resin or 15 a monomer unit from which the resin is produced by substituting hydrogen in the carboxylic group or alcoholic hydroxyl group of the resin or monomer unit with these groups. The monomer unit into which such a group was introduced may be copolymerized with the other monomer to produce the resin used in the present 20 invention.

In general, the resin used in the present invention preferably contains a polymerization unit having a butyrolactone residue in an amount within the range from 10 to 60% by mol of the total polymerization unit, although the range varies 25 depending on the kind of radiation for patterning exposure and kind of the group capable of cleaving by the action of the acid. The amount of the group capable of cleaving by an action of an acid is preferably within the range from 10 to 90% by mol of the

total polymerization unit. The polymerization unit having an alicyclic ring, which may or may not have the groups capable of cleaving by the action of the acid simultaneously, is preferably present in an amount of not less than 20% by mol of the total polymerization unit. This resin may also contains the other polymerization unit such as free carboxylic group as far as the effect of the present invention is not adversely affected.

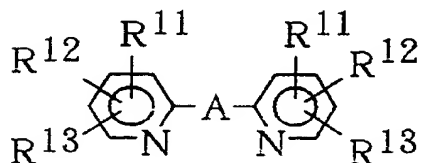
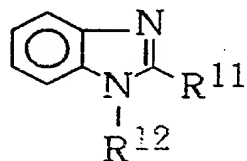
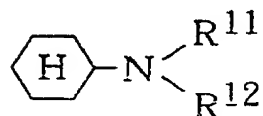
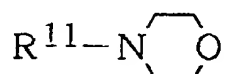
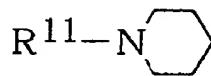
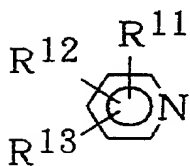
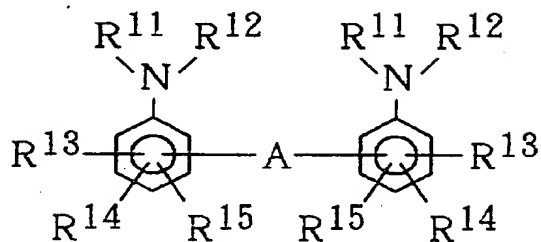
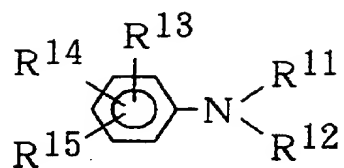
The acid generator, another component of the resist composition of the present invention, is a compound which is decomposed to generate an acid by exposing the compound itself or a resist composition containing the compound to radiation such as light and electron beam. The acid generated from the acid generator reacts with the resin, thereby to cleave the group capable of cleaving by an action of an acid. Examples of the acid generator include onium salt compound, organohalogen compound, sulfone compound and sulfonate compound. Specific examples thereof include the following compounds:

diphenyliodonium trifluoromethanesulfonate, 4-methoxyphenylphenyliodonium hexafluoroantimonate, 4-methoxyphenylphenyliodonium trifluoromethanesulfonate, bis(4-tert-butylphenyl)iodonium tetrafluoroborate, bis(4-tert-butylphenyl)iodonium hexafluorophosphate, bis(4-tert-butylphenyl)iodonium hexafluoroantimonate, bis(4-tert-butylphenyl)iodonium trifluoromethanesulfonate, triphenylsulfonium hexafluorophosphate, triphenylsulfonium hexafluoroantimonate, triphenylsulfonium trifluoromethanesulfonate, 4-methoxyphenyldiphenylsulfonium hexafluoroantimonate, 4-methoxyphenyldiphenylsulfonium

trifluoromethanesulfonate, p-tolyldiphenylsulfonium  
 trifluoromethanesulfonate, 2,4,6-  
 trimethylphenyldiphenylsulfonium trifluoromethanesulfonate,  
 4-tert-butylphenyldiphenylsulfonium  
 5 trifluoromethanesulfonate, 4-  
 phenylthiophenyldiphenylsulfonium hexafluorophosphate, 4-  
 phenylthiophenyldiphenylsulfonium hexafluoroantimonate, 1-  
 (2-naphthoylmethyl)thiolanium hexafluoroantimonate, 1-(2-  
 naphthoylmethyl)thiolanium trifluoromethanesulfonate, 4-  
 10 hydroxy-1-naphthyldimethylsulfonium hexafluoroantimonate, 4-  
 hydroxy-1-naphthyldimethylsulfonium  
 trifluoromethanesulfonate,  
 2-methyl-4,6-bis(trichloromethyl)-1,3,5-triazine, 2,4,6-  
 tris(trichloromethyl)-1,3,5-triazine, 2-phenyl-4,6-  
 15 bis(trichloromethyl)-1,3,5-triazine, 2-(4-chlorophenyl)-4,6-  
 bis(trichloromethyl)-1,3,5-triazine, 2-(4-methoxyphenyl)-  
 4,6-bis(trichloromethyl)-1,3,5-triazine, 2-(4-methoxy-1-  
 naphthyl)-4,6-bis(trichloromethyl)-1,3,5-triazine, 2-  
 (benzo[d][1,3]dioxolan-5-yl)-4,6-bis(trichloromethyl)-1,3,5-  
 20 triazine, 2-(4-methoxystyryl)-4,6-bis(trichloromethyl)-  
 1,3,5-triazine, 2-(3,4,5-trimethoxystyryl)-4,6-  
 bis(trichloromethyl)-1,3,5-triazine, 2-(3,4-  
 dimethoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine, 2-  
 (2,4-dimethoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-  
 25 triazine, 2-(2-methoxystyryl)-4,6-bis(trichloromethyl)-  
 1,3,5-triazine, 2-(4-butoxystyryl)-4,6-bis(trichloromethyl)-  
 1,3,5-triazine, 2-(4-pentyloxystyryl)-4,6-  
 bis(trichloromethyl)-1,3,5-triazine,

1-benzoyl-1-phenylmethyl p-toluenesulfonate, 2-benzoyl-2-  
 hydroxy-2-phenylethyl p-toluenesulfonate, 1,2,3-benzenetoluyyl  
 trimethanesulfonate, 2,6-dinitrobenzyl p-toluenesulfonate,  
 2-nitrobenzyl p-toluenesulfonate, 4-nitrobenzyl p-  
 5 toluenesulfonate,  
 diphenyl disulfone, di-p-tolyl disulfone,  
 bis(phenylsulfonyl)diazomethane, bis(4-  
 chlorophenylsulfonyl)diazomethane, bis(p-  
 tolylsulfonyl)diazomethane, bis(4-tert-  
 10 butylphenylsulfonyl)diazomethane, bis(2,4-  
 xylylsulfonyl)diazomethane,  
 bis(cyclohexylsulfonyl)diazomethane,  
 (benzoyl)(phenylsulfonyl)diazomethane, N-  
 (phenylsulfonyloxy)succinimide, N-  
 15 (trifluoromethylsulfonyloxy)succinimide, N-  
 (trifluoromethylsulfonyloxy)phthalimide, N-  
 (trifluoromethylsulfonyloxy)-5-norbornene-2,3-dicarboxyimide,  
 N-(trifluoromethylsulfonyloxy)naphthalimide and N-(10-  
 camphorsulfonyloxy)naphthalimide.

20 It is known that, in the chemical amplification type  
 positive resist composition, the performance deterioration due  
 to deactivation of the acid caused during standing after exposure  
 can be generally reduced by adding a basic compound, particularly  
 basic nitrogen-containing organic compound such as amines as a  
 25 quencher. In the present invention, it is also preferred that  
 such a basic compound is blended in the resist composition.  
 Specific examples of the basic compound used as the quencher  
 include those represented by the following respective formulas:



wherein  $R^{11}$ ,  $R^{12}$ ,  $R^{13}$ ,  $R^{14}$  and  $R^{15}$  independently represent hydrogen,  
 5 or an alkyl, cycloalkyl, aryl or alkoxy group which may be  
 substituted with a hydroxyl group; and A represents alkylene,  
 carbonyl or imino. The alkyl or alkoxy represented by  $R^{11}$  to  $R^{15}$   
 may have about 1 to 6 carbon atoms. The cycloalkyl represented  
 by  $R^{11}$  to  $R^{15}$  may have about 5 to 10 carbon atoms, and the aryl  
 10 represented by  $R^{11}$  to  $R^{15}$  may have about 6 to 10 carbon atoms.

The alkylene represented by A may have about 1 to 6 carbon atoms, and may be straight-chain or branched.

The resist composition of the present invention preferably comprises

5 the resin having a butyrolactone residue which may be optionally substituted with an alkyl as well as a group capable of cleaving by an action of an acid in an amount within the range from 80 to 99.9 and

an acid generator in an amount within the range from 0.1 to 20%  
10 by weight,

based on the weight of the whole solid content. When using a basic compound as the quencher, the resin composition preferably contains the basic compound in an amount within the range from 0.0001 to 0.1% by weight based on the weight of the whole solid  
15 content of the resist composition. This composition may also contains a small amount of various additives such as sensitizers, solubility inhibitors, other resins, surfactants, stabilizers, or dyes, if necessary.

The above respective components in the resist composition  
20 of the present invention is normally dissolved in a solvent to produce a resist solution, which is applied on a substrate such as silicon wafer. The solvent used herein may be any one which dissolves the respective components and has a suitable evaporation rate, and also imparts an uniform smooth film after  
25 evaporation of the solvent. This solvent may be a solvent which is normally used in this field. Examples thereof include glycol ether esters such as ethylcellosolve acetate, methylcellosolve acetate and propylene glycol monomethyl ether acetate; esters

such as ethyl lactate, butyl acetate, amyl acetate and ethyl pyruvate; ketones such as acetone, methyl isobutyl ketone, 2-heptanone and cyclohexanone; and cyclic esters such as  $\gamma$ -butyrolactone. These solvents may be use singly or in  
5 combination thereof.

A resist film obtained by applying a resist solution containing a resist composition of the present invention on a substrate and drying the resist solution is subjected to an exposure treatment for patterning, subjected to a heat treatment  
10 for accelerating a deblocking group reaction and then developed with an alkaline developer. The alkaline developer used herein may be various aqueous alkaline solutions used in this field, although an aqueous solution of tetramethylammonium hydroxide is widely used.

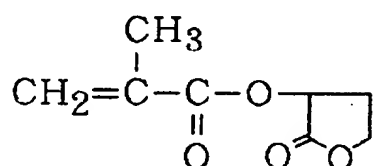
#### 15 EXAMPLES

The present invention will now be illustrated by means of the following Examples, which should not be construed to limit the scope of the invention. In the following Examples, "parts"  
20 are by weight unless otherwise stated.

#### Synthesis Example 1 (synthesis of a monomer)

$\alpha$ -bromo- $\gamma$ -butyrolactone (100 g) and methacrylic acid (104.4 g; i.e. 2.0 mol per mol of  $\alpha$ -bromo- $\gamma$ -butyrolactone) were  
25 charged, and, thereto, methyl isobutyl ketone was added in an amount which is three times by weight as that of  $\alpha$ -bromo- $\gamma$ -butyrolactone to prepare a solution. To the solution, triethylamine (183.6 g, i.e. 3.0 mol per mol of  $\alpha$ -bromo- $\gamma$ -

butyrolactone) was added dropwise, followed by stirring at room temperature for about 10 hours. After the resulting reaction mixture was filtered, the organic layer was washed with an aqueous 5 % by weight sodium hydrogencarbonate solution and then washed  
5 twice with water. Thereafter, the organic layer was concentrated to obtain  $\alpha$ -methacryloxy- $\gamma$ -butyrolactone represented by the following formula in yield of 85%.

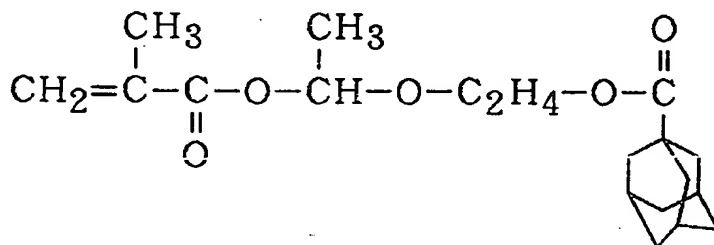


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#### Synthesis Example 2 (synthesis of another monomer)

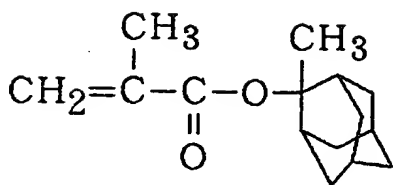
1-Adamantanecarbonyl chloride (55.1 g) and pyridine (44 g) were charged, and, thereto, methyl isobutyl ketone was added in an amount which is two times by weight as that of 1-  
15 adamantanecarbonyl chloride to prepare a solution. To the solution, ethylene glycol monovinyl ether (37.2 g, i.e. 1.5 mol per mol of 1-adamantanecarbonyl chloride) was added dropwise, followed by stirring at room temperature for about 10 hours. After the resulting reaction mixture was filtered, the organic  
20 layer was washed with an aqueous 5 % by weight sodium hydrogencarbonate solution and then washed twice with water. After the organic layer was concentrated, a three-fold amount (by weight) 1,4-dioxane was added to prepare a solution. In the solution, 0.8 g of p-toluenesulfonic acid monohydrate and  
25 methacrylic acid (36 g) were charged, followed by stirring at room temperature for about 10 hours. Thereafter, the organic

layer was washed with an aqueous 5 weight % sodium hydrogencarbonate solution and then washed twice with water. The organic layer was concentrated to obtain 1-  
 5 adamantanecarboxylic acid 2-(1-methacryloyloxyethoxy)ethyl represented by the following formula in yield of 75%.



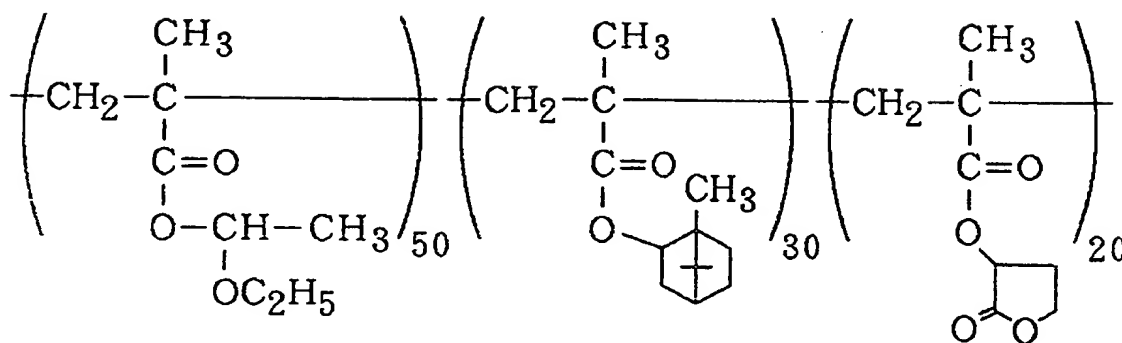
#### Synthesis Example 3 (synthesis of another monomer)

10 2-Methyl-2-adamantanol (83.1 g) and triethylamine (101 g) were charged, and, thereto, methyl isobutyl ketone (200 g) was added to prepare a solution. To the solution, methacrylic acid chloride (78.4 g, i.e. 1.5 mol per mol of 2-methyl-2-  
 15 adamantanol) was added dropwise, followed by stirring at room temperature for about 10 hours. After the resulting reaction mixture was filtered, the organic layer was washed with an aqueous 5 weight % sodium hydrogencarbonate solution and then washed twice with water. The organic layer was concentrated and then  
 20 distilled under reduced pressure to obtain 2-methyl-adamantyl methacrylate represented by the following formula in yield of 75%.



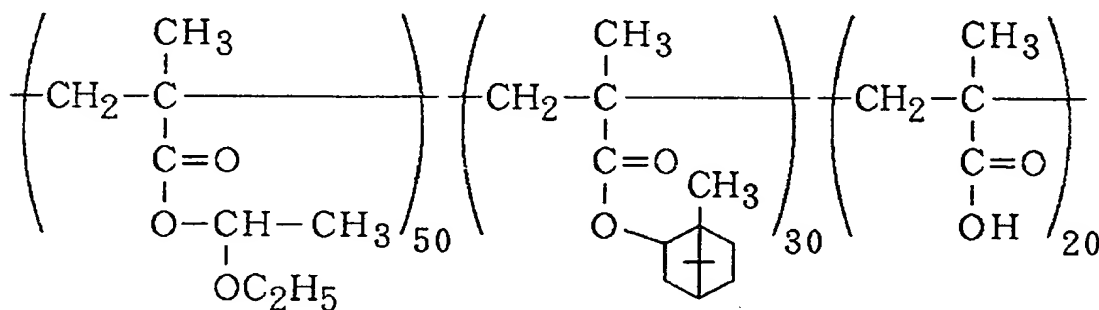
Synthesis Example 4 (synthesis of resin A1)

1-ethoxyethyl methacrylate, isobornyl methacrylate and  
 5  $\alpha$ -methacryloxy- $\gamma$ -butyrolactone obtained in Synthesis Example  
 1 were charged in a molar ratio of 5:3:2 (31.6 g : 26.7 g : 13.6  
 g), respectively, and methyl isobutyl ketone was added in an  
 amount which is two times by weight as that of the whole monomer  
 to prepare a solution. To the solution, azobisisobutyronitrile  
 10 as an initiator was added in an amount of 2% by mol based on the  
 whole monomer amount, followed by heating at 80 °C for about 8  
 hours. Thereafter, an operation of pouring the reaction  
 solution into a large amount of heptane to form a precipitate  
 was performed twice, followed by purification. As a result, a  
 15 copolymer represented by the following formula, wherein a  
 composition molar ratio of each unit is 50:30:20 and a  
 weight-average molecular weight measured by GPC with 230 nm UV  
 detector calculated as polystyrene is about 10,000, was  
 obtained.



Synthesis Example 5 (synthesis of resin AX: for comparison)

According to the same manner as that described in  
 5 Synthesis Example 4 except for 13.6 g of  $\alpha$ -methacryloxy- $\gamma$ -butyrolactone was replaced with 6.9 g of methacrylic acid (the molar ratio of 1-ethoxyethyl methacrylate : isobornyl methacrylate : methacrylic acid is 5:3:2), the operation was performed. As a result, a copolymer represented by the following  
 10 formula, wherein a composition molar ratio of each unit is 50:30:20 and a weight-average molecular weight measured by GPC with 230 nm UV detector calculated as polystyrene is about 10,000, was obtained.

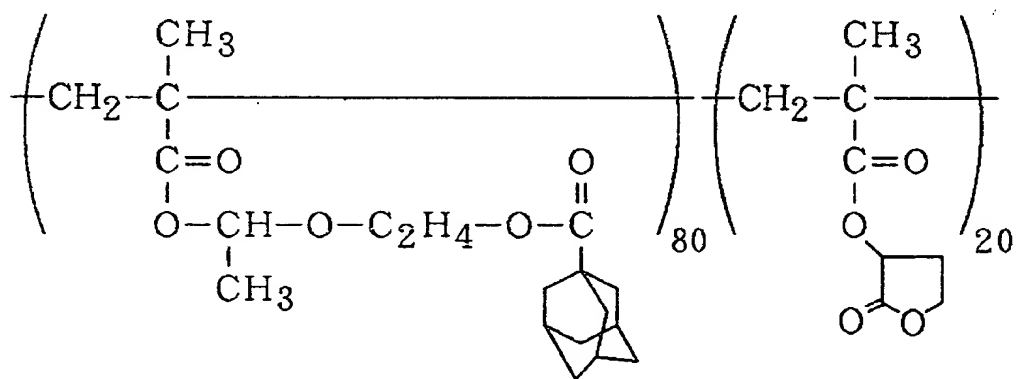


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Synthesis Example 6 (synthesis of resin A2)

1-adamantanecarboxylic acid 2-(1-

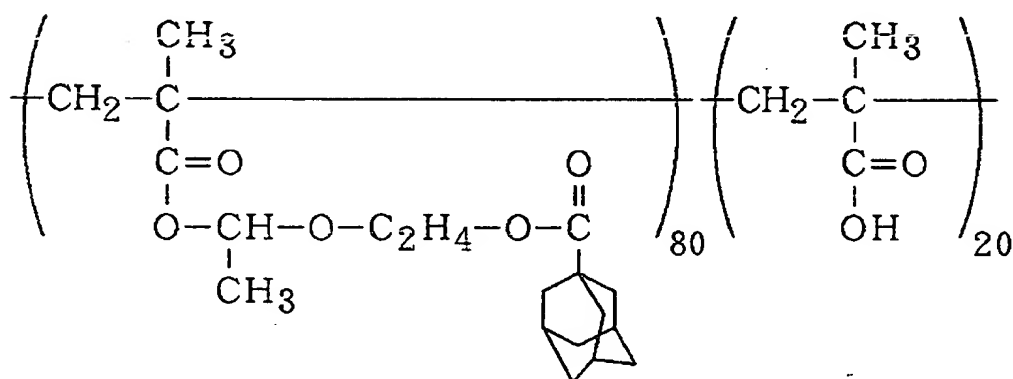
methacryloyloxyethoxy)ethyl obtained in Synthesis Example 2 and  $\alpha$ -methacryloxy- $\gamma$ -butyrolactone obtained in Synthesis Example 1 were charged in a molar ratio of 8:2 (33.7 g : 4.3 g). Thereto, methyl isobutyl ketone was added in an amount which is two times by weight as that of the whole monomer to prepare a solution. To the solution, azobisisobutyronitrile as an initiator was added in an amount of 2% by mol based on the whole monomer amount, followed by heating at 80 °C for about 8 hours. Thereafter, an operation of pouring the reaction solution into a large amount of heptane to form a precipitate was performed twice, followed by purification. As a result, a copolymer represented by the following formula, wherein a composition molar ratio of each unit is 80:20 and a weight-average molecular weight measured by GPC with 230 nm UV detector calculated as polystyrene is about 10,000, was obtained.



Synthesis Example 7 (synthesis of resin AY: for comparison)

According to the same manner as that described in Synthesis Example 6 except for 4.3 g of  $\alpha$ -methacryloxy- $\gamma$ -butyrolactone was replaced with 2.2 g of methacrylic acid (the

molar ratio of 1-adamantanecarboxylic acid 2-(1-methacryloyloxyethoxy)ethyl to methacrylic acid is 8:2), the operation was performed. As a result, a copolymer represented by the following formula, wherein a composition molar ratio of each unit is 80:20 and a weight-average molecular weight measured by GPC with 230 nm UV detector calculated as polystyrene is about 10,000, was obtained.



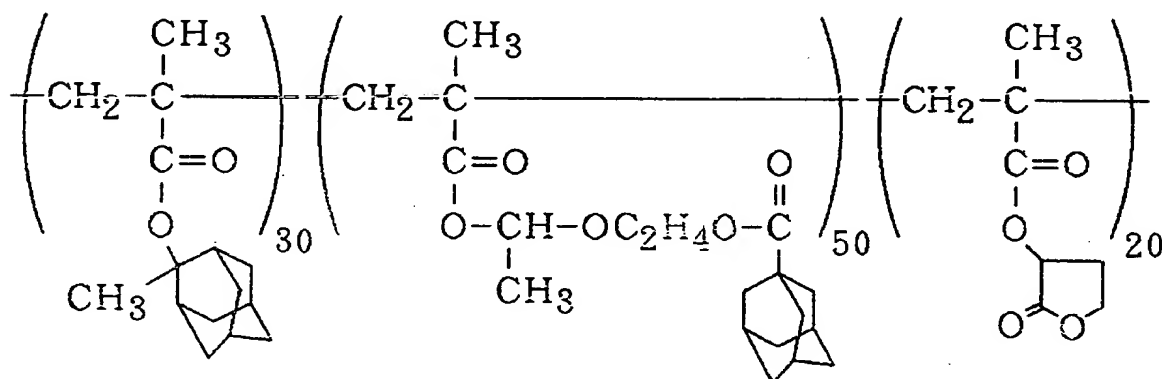
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#### Synthesis Example 8 (synthesis of resin A3)

2-methyl-2-adamantyl methacrylate obtained in Synthesis Example 3, 1-adamantanecarboxylic acid 2-(1-methacryloyloxyethoxy)ethyl obtained in Synthesis Example 2 and  $\alpha$ -methacryloxy- $\gamma$ -butyrolactone obtained in Synthesis Example 1 were charged in a molar ratio of 3:5:2 (23.4 g : 56.2 g : 11.3 g). Thereto, methyl isobutyl ketone was added in an amount which is two times as that of the whole monomer to prepare a solution. To the solution, azobisisobutyronitrile as an initiator was added in an amount of 2% by mol based on the whole monomer amount, followed by heating at 80 °C for about 8 hours. Thereafter, an operation of pouring the reaction solution into a large amount

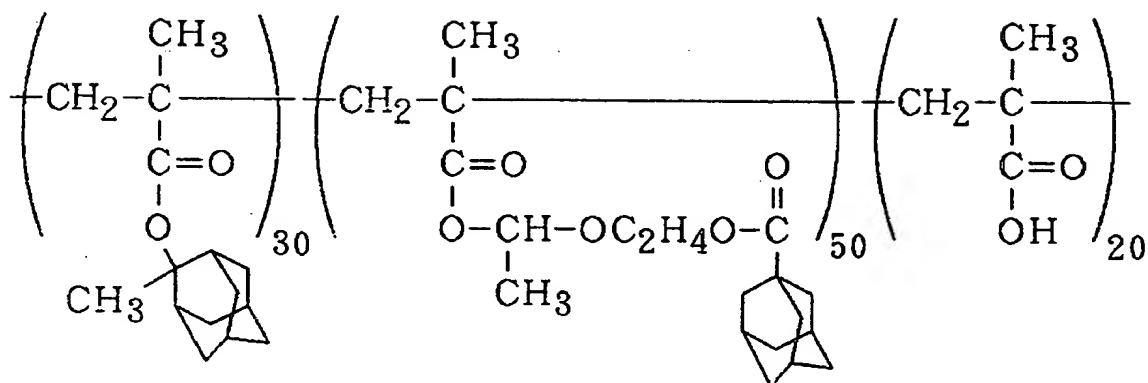
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of heptane to form a precipitate was performed twice, followed by purification. As a result, a copolymer represented by the following formula, wherein a composition molar ratio of each unit is 30:50:20 and a weight-average molecular weight measured by GPC with 230 nm UV detector calculated as polystyrene is about 10,000, was obtained.



# 10 Synthesis Example 9 (synthesis of resin AZ: for comparison)

According to the same manner as that described in Synthesis Example 8 except for 11.3 g of  $\alpha$ -methacryloxy- $\gamma$ -butyrolactone was replaced with 5.7 g of methacrylic acid (the molar ratio of 2-methyl-2-adamantyl methacrylate : 1-adamantanecarboxylic acid 2-(1-methacryloyloxyethoxy)ethyl : methacrylic acid is 3:5:2), the operation was performed. As a result, a copolymer represented by the following formula, wherein a composition molar ratio of each unit is 30:50:20 and a weight-average molecular weight measured by GPC with 230 nm UV detector calculated as polystyrene is about 10,000, was obtained.



# Examples 1 to 6 and Comparative Examples 1 to 6

In each of the Examples 1 to 6 and Comparative Examples 1 to 6, 15 parts of a resin shown in Table 1, 0.15 parts of diphenyldisulfone (manufactured by Midori Kagaku Co., Ltd.) as the acid generator and 0.01 parts of a quencher shown in Table 1 were dissolved in 60 parts of propylene glycol monomethyl ether acetate, and the resulting solution was filtered through a fluoro-resin filter having a pore diameter of 0.2  $\mu\text{m}$  to prepare a resist solution. This solution was coated, on a silicon wafer (contact angle of water: 60°) treated with hexamethyldisilazane (HMDS) or on a silicon wafer on which an organic anti-reflection coating was formed, so that a film thickness after drying became 0.72  $\mu\text{m}$ . The organic anti-reflection coating was formed by applying "XHRi-11" manufactured by Brewer Co. and baking under the conditions of 175°C for 60 seconds so that the thickness became 1700 Å. Prebaking after coating the resist solution was performed on a direct hot plate under the conditions of 90°C for 60 seconds.

Using a KrF excimer stepper ["NSR 1755 EX8A", NA=0.45, manufactured by Nikon Co., Ltd.], the wafer on which a resist

film was formed was exposed to form a line-and-space pattern.

A post exposure baking (PEB) was performed on a hot plate under the conditions shown in Table 1 and, furthermore, dip development was performed for 60 seconds by using a developer of an aqueous

5 2.38 weight % tetramethylammonium hydroxide solution or a developer prepared by diluting the solution with pure water as shown in Table 1. The pattern after development was observed by using a scanning electron microscope. The sensitivity and resolution were examined according to the following method,  
10 about the pattern obtained from the resist film formed on the organic anti-reflection coating substrate. The results are shown in Table 1.

Sensitivity: It was represented by an exposure dose at  
15 which a line-and-space pattern of  $0.5 \mu\text{m}$  becomes 1:1 (effective sensitivity)

Resolution: It was represented by a maximum dimension of a line-and-space pattern which is separated at an exposure dose of an effective sensitivity.

20

Using the pattern on the substrate on which organic anti-reflection coating was not formed, evaluation of the adhesion was performed at an exposure dose at which a line-and-space pattern of  $0.5 \mu\text{m}$  becomes 1:1. The results are shown  
25 in Table 1, wherein those keeping good adhesion are marked "○" and those causing peeling are marked "×".

Table 1

Example No.	Re-sin	Quen-cher	PEB condi-tion	Deve-loper	Effec-tive sensi-tivity	Resolu-tion	Adhe-sion
Example 1	A1	C1	100°C x 60 sec.	1/20	45 mJ/cm <sup>2</sup>	0.35 $\mu$ m	○
Example 2	A1	C1	100°C x 60 sec.	1/5	40 mJ/cm <sup>2</sup>	0.32 $\mu$ m	○
Example 3	A2	C2	60°C x 60 sec.	1/5	45 mJ/cm <sup>2</sup>	0.35 $\mu$ m	○
Example 4	A2	C2	60°C x 60 sec.	Not diluted	40 mJ/cm <sup>2</sup>	0.32 $\mu$ m	○
Example 5	A3	C2	70°C x 60 sec.	1/5	65 mJ/cm <sup>2</sup>	0.35 $\mu$ m	○
Example 6	A3	C2	70°C x 60 sec.	Not diluted	50 mJ/cm <sup>2</sup>	0.31 $\mu$ m	○
Compara-tive example 1	AX	C1	100°C x 60 sec.	1/20	30 mJ/cm <sup>2</sup>	0.40 $\mu$ m	○
Compara-tive example 2	AX	C1	100°C x 60 sec.	1/5	25 mJ/cm <sup>2</sup>	0.35 $\mu$ m	×
Compara-tive example 3	AY	C2	60°C x 60 sec.	1/5	30 mJ/cm <sup>2</sup>	0.40 $\mu$ m	○
Compara-tive example 4	AY	C2	60°C x 60 sec.	Not diluted	25 mJ/cm <sup>2</sup>	0.35 $\mu$ m	×
Compara-tive example 5	AZ	C2	70°C x 60 sec.	1/5	40 mJ/cm <sup>2</sup>	0.40 $\mu$ m	○
Compara-tive example 6	AZ	C2	70°C x 60 sec.	Not diluted	30 mJ/cm <sup>2</sup>	0.35 $\mu$ m	×

(Footnote of Table 1)

5 Quencher

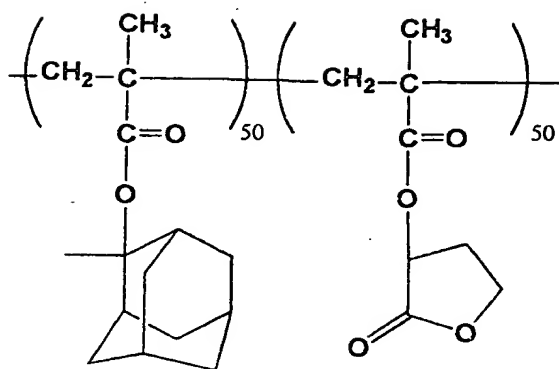
C1: N-phenyldiethanolamine

C2: 2,6-diisopropylaniline

Developer : dilution ratio (= 2.38 weight % tetramethylammonium  
5 hydroxide solution / pure water, by weight) are shown

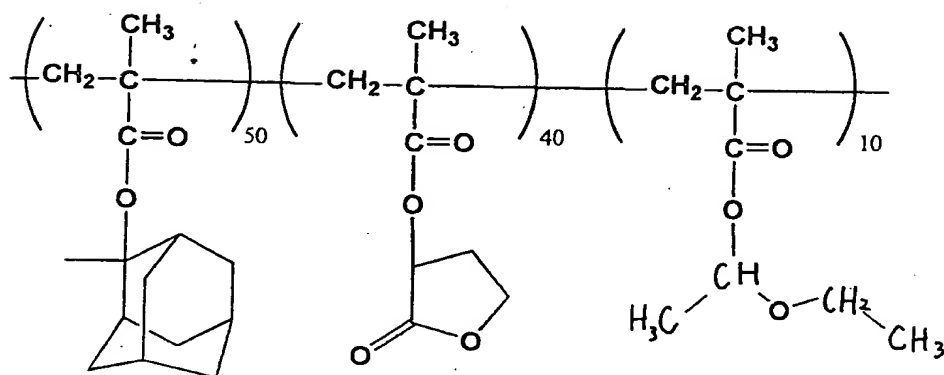
Synthesis Example 10 (synthesis of resin A4)

2-methyl-2-adamantyl methacrylate obtained in Synthesis  
Example 3 and  $\alpha$ -methacryloxy- $\gamma$ -butyrolactone obtained in  
10 Synthesis Example 1 were charged in a molar ratio of 5:5 (40.0  
g : 29.0 g). Thereto, methyl isobutyl ketone was added in an  
amount which is two times as that of the whole monomer to prepare  
a solution. To the solution, azobisisobutyronitrile as an  
initiator was added in an amount of 2% by mol based on the whole  
15 monomer amount, followed by heating at 80 °C for about 8 hours.  
Thereafter, an operation of pouring the reaction solution into  
a large amount of heptane to form a precipitate was performed  
twice, followed by purification. As a result, a copolymer  
represented by the following formula, wherein a composition  
20 molar ratio of each unit is 50:50 and a weight-average molecular  
weight measured by GPC with 230 nm UV detector calculated as  
polystyrene is about 8,000, was obtained.



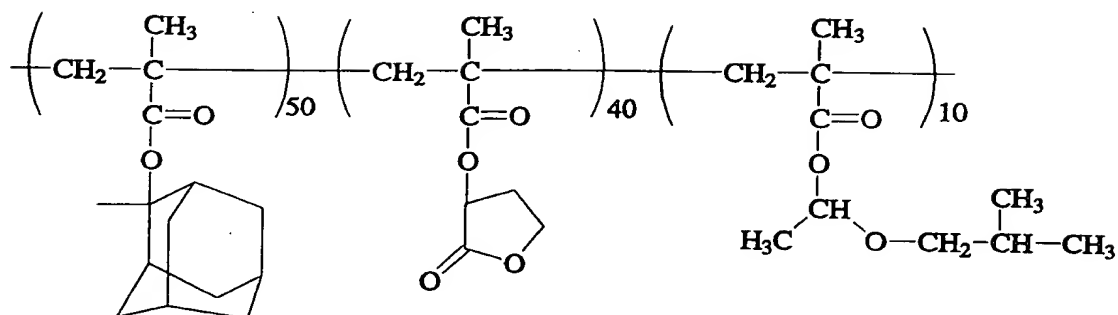
# Synthesis Example 11 (synthesis of resin A5)

2-methyl-2-adamantyl methacrylate obtained in Synthesis  
 5 Example 3,  $\alpha$ -methacryloxy- $\gamma$ -butyrolactone obtained in  
 Synthesis Example 1 and 1-ethoxyethylmethacrylate were charged  
 in a molar ratio of 5:4:1 (40.0 g : 23.2 g : 5.4 g). Thereto,  
 methyl isobutyl ketone was added in an amount which is two times  
 as that of the whole monomer to prepare a solution. To the  
 10 solution, azobisisobutyronitrile as an initiator was added in  
 an amount of 2% by mol based on the whole monomer amount, followed  
 by heating at 80 °C for about 8 hours. Thereafter, an operation  
 of pouring the reaction solution into a large amount of heptane  
 to form a precipitate was performed twice, followed by  
 15 purification. As a result, a copolymer represented by the  
 following formula, wherein a composition molar ratio of each unit  
 is 50:40:10 and a measured by GPC with 230 nm UV detector  
 calculated as polystyrene is about 8,000, was obtained.



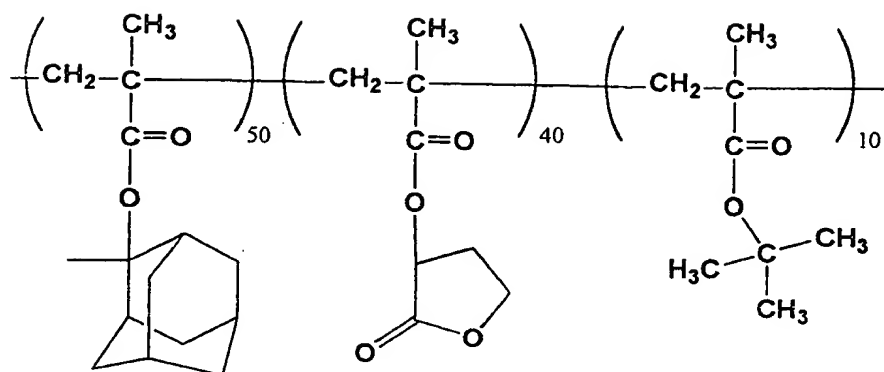
# Synthesis Example 12 (synthesis of resin A6)

2-methyl-2-adamantyl methacrylate obtained in Synthesis  
 5 Example 3,  $\alpha$ -methacryloxy- $\gamma$ -butyrolactone obtained in  
 Synthesis Example 1 and 1-isobutoxyethylmethacrylate were  
 charged in a molar ratio of 5:4:1 (40.0 g : 23.2 g : 6.4 g).  
 Thereto, methyl isobutyl ketone was added in an amount which is  
 two times as that of the whole monomer to prepare a solution.  
 10 To the solution, azobisisobutyronitrile as an initiator was  
 added in an amount of 2% by mol based on the whole monomer amount,  
 followed by heating at 80 °C for about 8 hours. Thereafter, an  
 operation of pouring the reaction solution into a large amount  
 of heptane to form a precipitate was performed twice, followed  
 15 by purification. As a result, a copolymer represented by the  
 following formula, wherein a composition molar ratio of each unit  
 is 50:40:10 and a weight-average molecular weight measured by  
 GPC with 230 nm UV detector calculated as polystyrene is about  
 8,000, was obtained.



### Synthesis Example 13 (synthesis of resin A7)

2-methyl-2-adamantyl methacrylate obtained in Synthesis  
 5 Example 3,  $\alpha$ -methacryloxy- $\gamma$ -butyrolactone obtained in  
 Synthesis Example 1 and t-butylmethacrylate were charged in a  
 molar ratio of 5:4:1 (40.0 g : 23.2 g : 4.8 g). Thereto, methyl  
 isobutyl ketone was added in an amount which is two times as that  
 of the whole monomer to prepare a solution. To the solution,  
 10 azobisisobutyronitrile as an initiator was added in an amount  
 of 2% by mol based on the whole monomer amount, followed by heating  
 at 80 °C for about 8 hours. Thereafter, an operation of pouring  
 the reaction solution into a large amount of heptane to form a  
 precipitate was performed twice, followed by purification. As  
 15 a result, a copolymer represented by the following formula,  
 wherein a composition molar ratio of each unit is 50:40:10 and  
 a measured by GPC with 230 nm UV detector calculated as  
 polystyrene is about 8,000, was obtained.



#### Examples 7 to 10

In each of the Examples 7 to 10, 15 parts of a resin shown  
 5 in Table 1, 0.30 parts of 4-methylphenyldiphenylsulfonium  
 trifluoromethanesulfonate (manufactured by Midori Kagaku Co.,  
 Ltd.) as the acid generator and 0.02 parts of a quencher shown  
 in Table 1 were dissolved in 70 parts of propylene glycol  
 monomethyl ether acetate, and the resulting solution was  
 10 filtered through a fluoro-resin filter having a pore diameter of  
 0.2  $\mu\text{m}$  to prepare a resist solution. This solution was coated,  
 on a silicon wafer (contact angle of water:  $60^\circ$ ) treated with  
 hexamethyldisilazane (HMDS) or on a silicon wafer on which an  
 organic anti-reflection coating was formed, so that a film  
 15 thickness after drying became 0.455  $\mu\text{m}$ . The organic anti-  
 reflection coating was formed by applying "DUV-18L" manufactured  
 by Brewer Co. and baking under the conditions of  $215^\circ\text{C}$  for 60  
 seconds so that the thickness became 570  $\text{\AA}$ . Prebaking after  
 coating the resist solution was performed on a direct hot plate  
 20 under the conditions of  $130^\circ\text{C}$  for 60 seconds.

Using the resist film thus obtained, according to  
 conditions shown in Table 2 and according to same manner as in

Example 1-6, the sensitivity and resolution were examined and evaluation of the adhesion was performed. The results are shown in Table 2.

5 Table 2

Example No.	Re-sin	Quen-cher	PEB condi-tion	Deve-loper	Effec-tive sensi-tivity	Resolu-tion	Adhe-sion
Example 7	A4	C2	120°C x 60 sec.	Not diluted	80 mJ/cm <sup>2</sup>	0.24 μm	○
Example 8	A5	C2	120°C x 60 sec.	Not diluted	70 mJ/cm <sup>2</sup>	0.23 μm	○
Example 9	A6	C2	120°C x 60 sec.	Not diluted	60mJ/cm <sup>2</sup>	0.22 μm	○
Example 10	A7	C2	120°C x 60 sec.	Not diluted	75 muj/cm <sup>2</sup>	0.24 μm	○

(Footnote of Table 1)

Quencher

C1: N-phenyldiethanolamine

10 C2: 2,6-diisopropylaniline

As shown in Table 1 and 2, the resist composition of the present invention does not cause peeling at the time of developing even if the concentration of the developer is high, and is superior in adhesion to the substrate. The resolution is also improved and the sensitivity is not drastically deteriorated. Each of compositions used in Examples 1 to 6 gives a resist pattern having excellent performances even by the exposure using an ArF excimer laser aligner.

20 The chemical amplification type positive resist

composition of the present invention is superior in adhesion to a substrate and is also superior in various resist performances such as resolution. Accordingly, this composition is suitable for exposure using KrF excimer laser, ArF excimer laser, and the  
5 like, thereby to obtain a resist pattern having high performance.